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LABORATORY EVALUATION OF THE PROTOCOL FOR THE VOLATILE ORGANIC SAMPLING TRAIN

Thomas J. Logan, Robert G. Fuerst, M. Rodney Midgett
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina

and

John Prohaska,
PEI Associates, Inc.
Cincinnati, Ohio.

EPA Contract 68-02-3767

The measurement of volatile organic emissions from a hazardous waste incinerator is one of the more difficult source testing problems. Specific compounds called principal organic hazardous constituents (POHC) are to be identified and quantified at levels of 0.5 to 100 ppb in hot, wet incinerator exhaust gas, which may also contain high particulate and acid levels. The protocol, which describes the practices used by laboratories making these measurements, allows for several alternative designs and operating procedures. This paper describes an experimental program to evaluate under controlled conditions in the laboratory as many of the acceptable practices as possible. It describes the results of sampling at various concentration levels using two tube configurations, two moisture levels and other procedural variations. These results have led to conclusions about the specific VOST procedures to be followed during the field validation studies.

INTRODUCTION

The Code of Federal Regulation, Title 40, Part 264, requires that a destruction and removal efficiency (DRE) of 99.99 percent be achieved for each principal organic hazardous constituent (POHC) designated in the Trial Burn Permit (1). The calculation of DRE requires sampling and analysis to quantify POHCs in the waste feed material and stack gas effluent. The "Sampling and Analysis Methods for Hazardous Waste Combustion" manual provides information on methods that are applicable for collection and analyses of POHCs in process streams of hazardous waste incinerator units (2). The "Protocol for the Collection and Analysis of Volatile POHCs using VOST" (VOST Protocol) describes the Volatile Organic Sampling Train (VOST) used to measure POHCs in the stack gas effluent (3).

The purpose of this paper is to describe a laboratory study conducted by EPA to evaluate the VOST Protocol. This work was undertaken prior to the field validation to be sure that the best set of procedures would be validated in the field effort. The project was done under contract by PEI Associates in Cincinnati, Ohio, who developed the specific equipment and procedures for the laboratory study. The work was supported by the Quality Assurance Division (QAD), Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

EXPERIMENTAL

Six volatile organic compounds were selected for use in the VOST laboratory evaluation. These compounds are listed in Table I. This table shows the compounds' boiling points and incinerability. Two of these compounds, carbon tetrachloride and chloroform, were included because of their expected frequent designation as principal organic hazardous constituents (POHC) in hazardous waste incinerator trial burns. Benzene was included because of the effect its historically high background levels has had on Tenax, which is the primary sample collection medium of the VOST. Tetrachloroethylene or perchloroethylene (commonly referred to as "perc") was included in the study to test recovery of a compound with a boiling point (121°C) near the high range of the protocol (approximately 100°C). Trichlorofluoromethane (TCFM) was selected because its low boiling point (24°C) challenged the recovery of the VOST. The final compound studied in this investigation was vinyl chloride (VC). VC was included even though its boiling point (-12°C) made it unlikely to be quantitatively recovered by the VOST. Except for TCFM, mixtures of these compounds at the ppb level were readily available as Group 1 gases through the QAD gas cylinder audit development program. The QAD's Group 1 gases were developed and certified by the National Bureau of Standards (NBS) and, therefore, concentrations of these mixtures could be traced to NBS for use in determining VOST recovery. A separate cylinder containing only TCFM and nitrogen was obtained, and the concentration of this cylinder was similarly traced to an NBS standard.

Test gas atmospheres for the laboratory study were generated by mixing gases from a cylinder of the five Group 1 gases (approximately 75 ppb each component, balance nitrogen), a cylinder of approximately 75 ppb TCFM in nitrogen, and a cylinder of ultra-pure zero air. At the conclusion of the project, the cylinders containing these compounds were anlyzed independently by Research Triangle Institute (RTI) to verify labeled cylinder values and the stability of the low-level gases over the duration of the project. No values differed by more than 10 percent. The dilution system used to mix the gases was checked for leaks, levels of contamination and

stability of operation and found to be acceptable before any test samples were collected.

The dilution system and cylinder gases were used to generate test gas concentrations of approximately 15 and 0.5 ppb. These two concentrations were considered to be within the range of normal hazardous waste incinerator POHC concentrations.

A quad (four-train) VOST was used to collect four samples simultaneously from a manifold purged with test gas of known levels of target compounds. Figure 1 shows a schematic of the quad VOST equipment in the laboratory evaluation. Figure 2 shows a more detailed description of a single VOST. Two types of VOST sample collection tubes are specified in the VOST Protocol. Figure 3 shows the two tube configurations in detail. The term "ST" is used in this report to designate the suspended tube design, which has numerous other names since it is the tube conventionally used in ambient air sampling with Tenax. The other design is designated "ND" for neck-down tube. The VOST Protocol defines the ND the inside/inside tube configuration and the ST as the inside/outside tube configuration. Since one of the goals was to determine which design to use in field work, the quad VOST experiments were conducted with two ST-type trains and two ND-type trains.

All sampling activities were conducted in a mobile laboratory separate from the analysis and sorbent preparation areas.

The sorbent traps were all prepared from one lot of Tenax and one lot of charcoal and were prepared and conditioned as specified in the protocol. Preparation and conditioning of the traps were performed in a separate area of the laboratory in which no solvents are handled or stored. The exact handling of each trap during preparation and conditioning activities was documented in a log book.

Each pair of traps was blank-checked as a unit following conditioning and prior to use. The blanking procedure consisted of thermally desorbing the traps, concentrating the blank sample cryogenically, flash-vaporizing the concentrated sample, and analyzing the sample by gas chromatography/flame ionization detection (GC/FID). Because the GC/FID procedure gave only a general indication of blank levels, 1 of each 10 trap pairs was analyzed as a sample by gas chromatography/mass spectrometry (GC/MS) instead of GC/FID to determine actual blank levels of all the target compounds. Except for benzene, the blank levels for all other compounds were less than 10 nanograms per pair of traps.

All sorbent traps were analyzed in the same manner and in accordance with the protocol. Each sampled trap was spiked with an internal standard, thermally desorbed with organic-free helium gas bubbled through organic-free water and collected on an analytical sorbent trap. After the sample desorption steps, the analytical sorbent trap was rapidly heated and the carrier gas flow was reversed so the the effluent flow from the analytical trap was directed into the GC/MS. The volatile organics were separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The mass of volatile compounds was calculated by the internal standard technique.

Unless specifically designated otherwise, all samples were analyzed within one week of collection.

The front (Tenax) and back (Tenax/charcoal) sorbent traps were analyzed separately for each sample run to determine in which portion of the train the target compounds were actually collected and to assess the potential for breakthrough.

RESULTS

In the course of performing the laboratory evaluation, several parameters were studied (sorbent tube design, moisture level in the sample gas and sample holding time).

The effects of tube design and moisture level varied from one component to the next and have been evaluated on a component basis. The following discussion describes the individual component data presented in Table II, which was summarized from eight quad VOST runs.

The sample means are simple averages of paired run data; standard deviations are pooled from paired run data. The percent relative standard deviation (RSD) values represent the pooled standard deviations expressed as a percent of the means. The percent expected value (EV) is the mean measured concentration expressed as a percent of the concentration of the target compound in the sampled gas stream. The statistical significance of the difference between the paired measurement results for each type of sampling train was determined by analysis of variance (ANOVA) for the dry test runs. The statistical significance of any difference between train types for the wet runs was determined by use of the t-test. Differences between train-types were determined to be statistically significant if the respective test indicated there was less than a 10 percent probability the difference was due to chance.

Vinyl Chloride--

An examination of the data at each test condition incidated that the ST sampling trains were ineffective in all cases. The maximum amount of vinyl chloride (VC) recovered by use of the ST train was 60 percent of the expected value for one of the wet runs at 15 ppb. Only the ND results at the 15 ppb dry test conditions were considered reasonable, with an average recovery of 91 percent EV. Unfortunately, subsequent experiments could not reproduce the 91 percent EV for VC. The presence of approximately 30 percent moisture in the test gas had a different effect on the two types of trains. The apparent effect on the ST results was to improve the average recovery. The effect of moisture was definitely detrimental to the ND train results at 15 ppb in that the average recovery was decreased from 91 to 48 percent EV.

RSD values were used as estimates of precision. The best and worst RSD values were for the ST trains at dry test gas conditions; however, these values were considered nonrepresentative because of very low recoveries. Pooled precision values for the ND train type ranged from 7 to 10 percent RSD at 15 ppb.

Trichlorofluoromethane--

The statistical tests showed a significant difference between the results determined with the two types of sampling trains for the high concentration of test gas (i.e., 15 ppb) for both wet and dry test gas conditions. In both cases the highest concentration of TCFM was reported

for the ND sampling train. At the 0.5 ppb level, the results reported for the two types of sampling trains agreed quite well.

Examination of the TCFM data indicated that the presence of moisture in the test gas affected only the ST trains at the 15 ppb level. The average recovery by the ST trains was 56 percent EV for the dry test runs versus 39 percent EV for the wet runs at 15 ppb. Conversely, the average recovery by the ND trains was approximately 75 percent EV for both wet and dry runs at 15 ppb.

The precision of the pooled data in each of the four test conditions ranged from 6 to 14 percent RSD for the ND trains. Precision of the pooled ST data was much more variable, ranging from 40-60% RSD.

Chloroform--

The statistical analyses indicate that the difference between the measurements made by the two types of sampling trains was significant only for the 15-ppb wet gas. For this test condition, the average concentration measured by the ND trains was 73.34 ng/liter compared with 65.31 ng/liter for the ST trains, for a difference of approximately 11 to 12 percent between the types of trains. Although the statistical comparison indicated the probability that this difference was due to chance was less than 5 percent, a difference of 12 percent does not seem significant when compared to overall results including other compounds.

An examination of the data sets indicated the presence of moisture in the test gas did not affect results obtained by the use of either type of train.

Precision of the pooled data sets at each condition for the ND trains varied between 4 and 23 percent RSD. Precision of the pooled data sets at each test condition for the ST trains varied between 3 and 15 percent RSD.

Carbon Tetrachloride--

The statistical analyses indicated that the results reported for the ND trains were significantly higher than those reported for the ST trains at all of the nominal test conditions except the 15-ppb dry gas.

An examination of the data sets indicated that the presence of approximately 30 percent moisture by volume in the test gas had no effect on the performance of the ND trains but definitely had an adverse effect on the recovery of the ST trains. The average recovery for the ST trains at 0.5 ppb was 71 percent EV dry test condition compared with 51 percent EV wet test condition, and at the 15-ppb test condition recoveries were 78 and 56 percent EV at dry and wet test conditions, respectively. By comparison, the average recoveries of the ND trains ranged from 85 to 92 percent EV for all test conditions.

Precision of the pooled data sets at each test condition for the ND trains ranged from 1 to 28 percent, RSD.

Benzene--

The statistical analyses determined that the difference between the results reported for the two types of sampling trains was not statistically significant at any of the four nominal test conditions.

An examination of the data at each test condition indicated that the presence of moisture in the test gas may have had some effect on the results measured by each type of train, but the differences between the dry and wet data were similar to the differences between train-types (which were determined not to be significant).

The very high recovery values obtained by both types of trains at the 0.5-ppb test conditions may be related to inherent benzene contamination, either because of inconsistent pretest conditioning effects or sorbent degradation after the conditioning procedure. The overall average recovery at 0.5-ppb conditions was approximately 150 percent EV. Average recoveries at the 15-ppb test conditions were not as high as those for the 0.5-ppb test gas and ranged from 100 to 116 percent EV.

The precision of the test results was also worse for the low-level tests than for the high-level tests. At 0.5 ppb, the precision of the pooled data sets varied between 2 and 44 percent RSD. For the tests conducted at 15 ppb, the pooled precision varied between 2 and 27 percent RSD.

Tetrachloroethylene--

The statistical tests showed that there was no significant difference between the tetrachloroethylene (perc) concentrations reported for the two types of sampling trains.

An examination of the data at each condition indicated the presence of moisture in the test gas did not affect the ability of either type of sampling train to measure concentrations of perc. The average recovery values were higher at the 15-ppb test conditions than at the 0.5-ppb test conditions, ranging from 108 to 133 percent EV and from 100 to 109 percent EV, respectively.

Precision values ranged from 1 to 46 percent RSD for the pooled data sets at 0.5 ppb and from 3 to 25 percent RSD for the pooled data sets at 15 ppb.

EFFECT OF SAMPLE HOLDING TIME

All samples for quad Runs Q1, Q2, and Q3 were analyzed in the laboratory within less than one week after sample collection. Samples from quad Run Q4 were analyzed two weeks after sample collection and those from quad Run Q5 were analyzed five weeks after collection. All of these samples were collected during the same week of sampling and at the same nominal test conditions, 15-ppb concentration of target compounds in a dry gas stream. The measured concentration data were analyzed statistically by ANOVA to determine if the difference between results obtained at the three sample holding times was significant. For example, the average concentration of VC for Run Q5 (5-week holding time) was compared with the average concentration of VC for Run Q4 (2-week holding time) and for Runs Q1, Q2, and Q3 (holding time less than 1 week). If the difference between the concentration was significant, the effect of holding time was significant. A summary of the results of the analysis of the effect of holding time is presented in Table III.

As can be seen from Table III, there was an overall tendency toward a decrease in the reported concentration of each target compound as the time between sample collection and sample analysis was increased. The value obtained for any compound on either type of trap, except VC on ST traps,

was the highest when analysis was completed within 1 week. This apparent effect of sample holding time was statistically significant for vinyl chloride and trichlorofluoromethane, the two lowest-boiling compounds studied.

For TCFM, a decrease in concentration of approximately 25 percent within two weeks of collection for the ND trains indicates that samples should be analyzed as soon as possible after collection. Again, the ST trains were not very effective because of low recovery (~56% EV as shown in Table II). The similarity between results at the 2- and 5-week holding times seems to indicate that any significant loss of TCFM occurs within the first two weeks.

It should be noted that these results are for high-level (~15 ppb), dry samples, which may be "ideal" samples. The effect of sample holding time will also be investigated for actual field samples.

CONCLUSIONS

The laboratory evaluation indicates that the precision and accuracy of the VOST protocol depends on the target compound and on the type of sorbent trap used. In some cases, the precision and accuracy may also be affected by the moisture content of the sample stream and the amount of compound collected on the sorbent trap. The amount collected is a function of the concentration in the sample stream, the sampling rate, the sample volume, and the sampling time.

The most obvious conclusion of the laboratory tests is that neither the ND- nor ST-type of sorbent trap designs produced acceptable results for vinyl chloride.

The precision and accuracy for the ND and the ST types of sorbent traps varied for each compound and must, therefore, be described individually. For example, of the three compounds -- chloroform, carbon tetrachloride and tetrachloroethylene -- only carbon tetrachloride showed differences in precision and accuracy between the ND and ST traps. For carbon tetrachloride, the ST traps also showed differences between wet and dry conditions. The ND traps showed no differences between wet and dry conditions.

Benzene results must be considered separately because of the inherent problem of benzene presence in the Tenax sorbent. At concentrations of 15 or 0.5 ppb, no distinguishable effect was observed for trap type or moisture condition; however, the amount collected had a definite effect. Average benzene recoveries were 108 and 155 percent, with corresponding precision estimates of 16 and 35 percent, for collections of approximately 1000 and 50 ng, respectively. Precision and accuracy results for benzene were not comparable to those for the other compounds when less than approximately 50 ng were collected in the sample.

The ND data for trichlorofluoromethane and carbon tetrachloride and all the data for chloroform and tetrachloroethylene indicate that average recoveries for the four compounds ranged from 75 to 121 percent. Precision (expressed as the pooled RSD of the replicate pairs) varied between 8 and 23 percent at the two different concentrations under both wet and dry conditions when approximately 50 ng or more of each compound was collected.

With the possible exception of benzene, the estimates of accuracy obtained during this laboratory study (75 to 121 percent) were better than that given in the VOST Protocol (50 to 150 percent). The precision estimates (23 percent or better) are considered good. Because these estimates were obtained on a clean air matrix, they cannot be considered typical of actual test site precision and accuracy.

In general, the results indicate that the ND traps were superior to the ST traps. The ND traps are less complicated in design and handling and have a positive forced flow during desorption; therefore, their performance should be as good as or superior to that of the ST traps for other, untested, compounds.

A trend toward lower recoveries with prolonged holding times was observed for all compounds included in this study. Excluding vinyl chloride, the only compound for which the lower recovery could be considered significant was trichlorofluoromethane, which showed approximately a 30 percent decrease on both types of traps when samples were analyzed 2 weeks after collection. Again, these results were obtained on a matrix of clean, dry air; the effect of holding time may increase under actual field conditions.

RECOMMENDATIONS

The recommended changes to the VOST Protocol have been described in detail in the PEI Laboratory Report on the VOST. Recommendations for minor modifications to the VOST Protocol were made in the following areas:

- Calibration procedure for the dry gas meter.
- Field blank handling.
- Substitution of methanol instead of pentane for extraction of glass wool.
- Elimination of methanol extraction of charcoal.
- Prescreening of charcoal prior to its use in traps.
- Prescreening of each lot of Tenax.
- Predrying of Tenax before it is placed in the vacuum oven.
- More specific procedures for sorbent trap conditioning to enhance consistency of blank levels, including longer conditioning time and maintenance of positive flow during heating and cooling.
- Specific procedures for handling conditioned traps to minimize ambient air contamination.
- More sensitive and specific calibration for blank checking.
- More specific procedures for blank checking.
- Quality control for blank checking, including system blanks and recovery checks.
- Different sample desorption flow rate.

- Development of a procedure for evaluating performance of the analytical trap in the purge and trap apparatus.
- Addition of a recovery check procedure for the analytical system.
- Development of procedures for determining acceptable analytical separation to assist in column selection and other GC conditions.
- Development of procedures for determining appropriate calibration levels.

Overall, the laboratory evaluation accomplished all of its stated objectives.

REFERENCES

1. Code of Federal Regulations, Title 40, Part 264 (1980).
2. Harris, J. C., et al, "Sampling and Analysis Methods for Hazardous Waste Combustion," EPA 600/8-84-002, February 1984.
3. Hansen, E. M., "Protocol for the Collection and Analysis of Volatile POHCs Using VOST," EPA 600/8-84-007, March 1984.

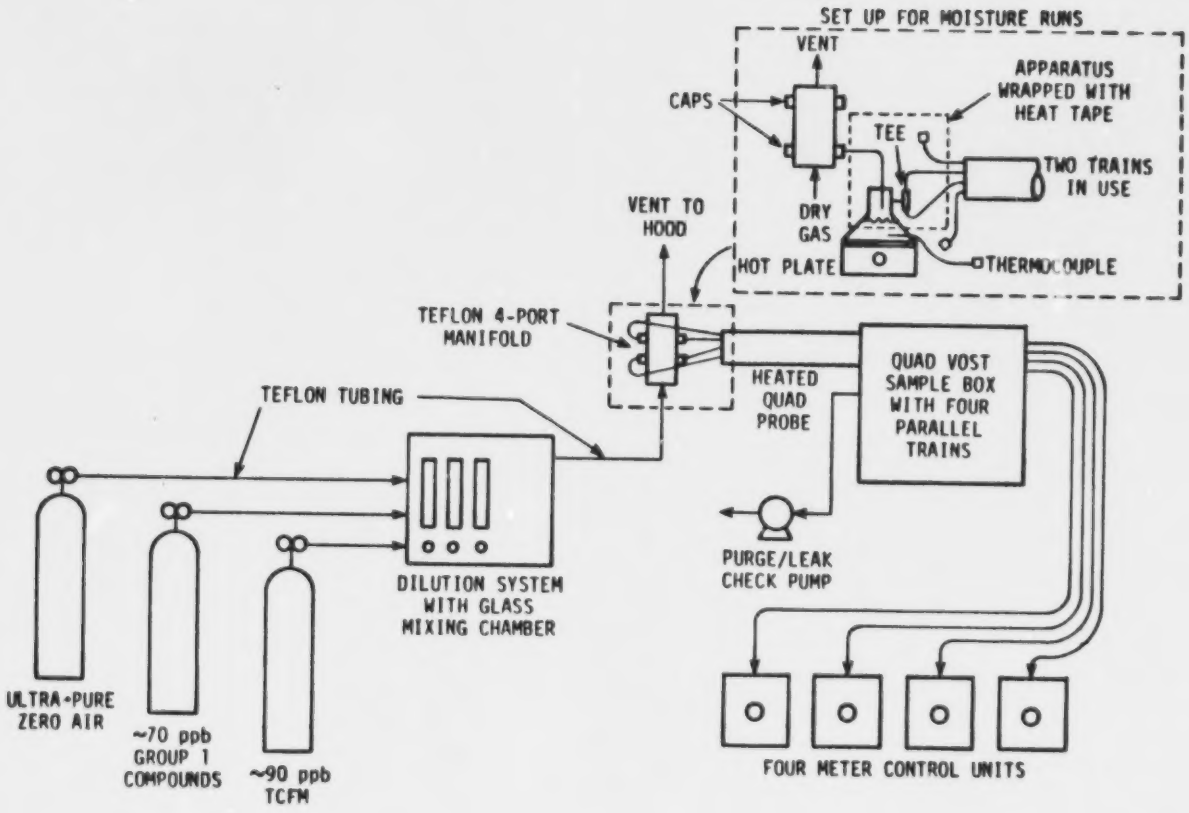

Figure 1. Schematic of sampling arrangement for laboratory evaluation.

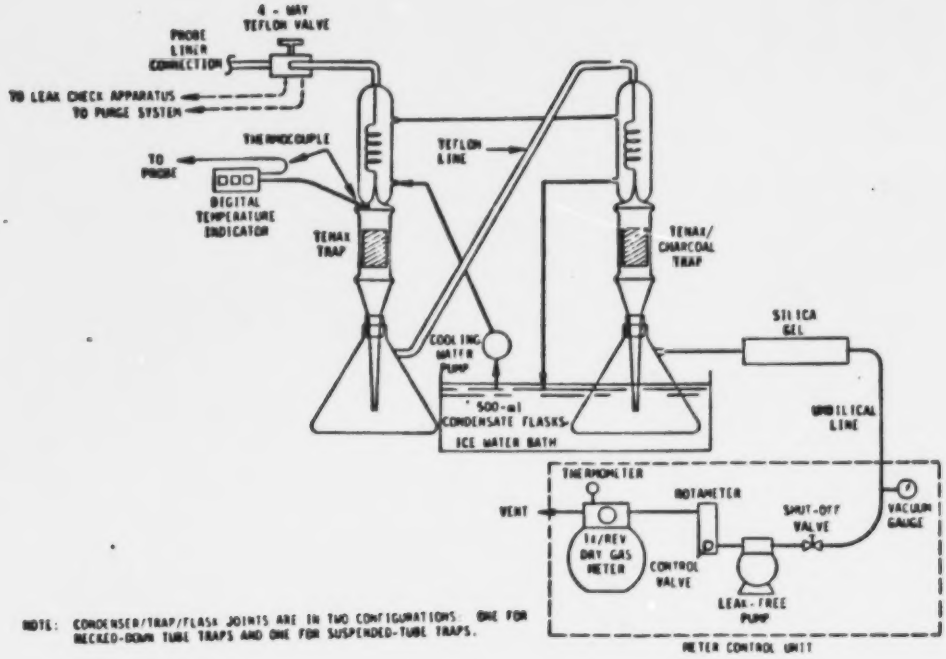

Figure 2. Schematic of single volatile organic sampling train (VOST).

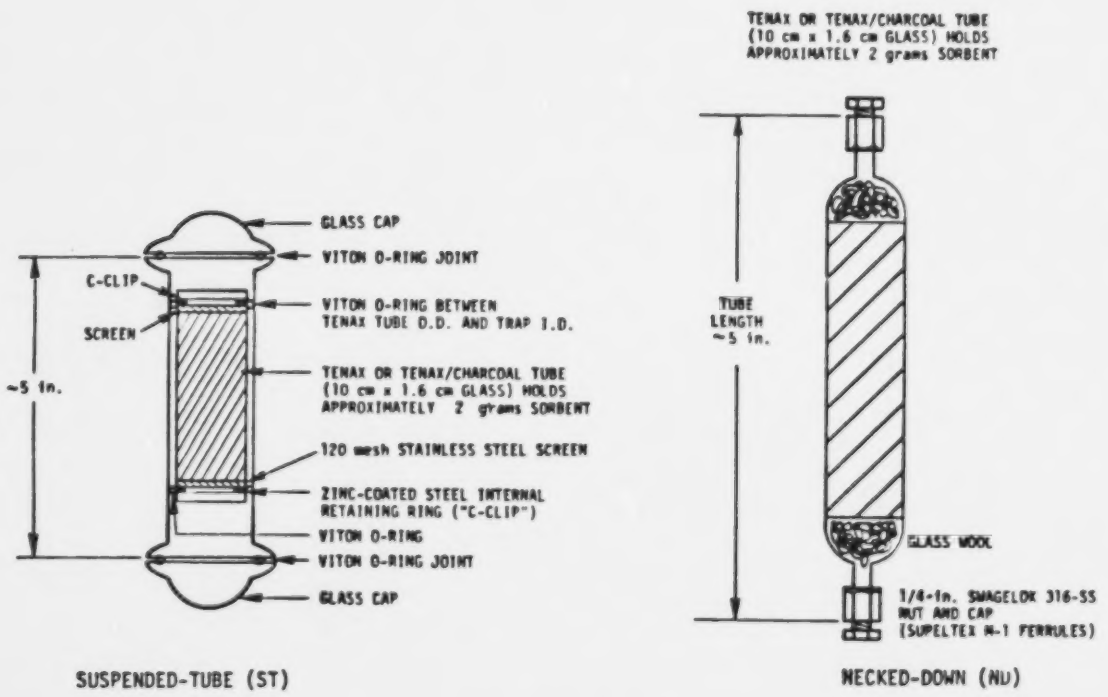
GLASS CAP
VITON O-RING JOINT
C-CLIP
SCREEN
VITON O-RING BETWEEN TENAX TUBE O.D. AND TRAP I.D.
~5 in.
TENAX OR TENAX/CHARCOAL TUBE (10 cm x 1.6 cm GLASS) HOLDS APPROXIMATELY 2 grams SORBENT
120 mesh STAINLESS STEEL SCREEN
ZINC-COATED STEEL INTERNAL RETAINING RING ("C-CLIP")
VITON O-RING
VITON O-RING JOINT
GLASS CAP
SUSPENDED-TUBE (ST)
TENAX OR TENAX/CHARCOAL TUBE (10 cm x 1.6 cm GLASS) HOLDS APPROXIMATELY 2 grams SORBENT
TUBE LENGTH ~5 in.
GLASS WOOL
1/4-in. SWAGELOK 316-SS NUT AND CAP (SUPELTEX M-1 FERRULES)
NECKED-DOWN (NU)

Figure 3. Sorbent trap configurations.

TABLE I. LIST OF COMPOUNDS SELECTED FOR VOST PROTOCOL VALIDATION

Compound	Boiling point,[b] °C	Incinerability[a] ranking		Comments
		ΔH[c]	T 99.99/2[d]	
Tetrachloroethylene	121	15	1	Group 1 compound;[e] potential recovery problem
Benzene	80	282	23	Group 1; historical Tenax blank problem
Carbon tetrachloride	77	4	2	Group 1; frequently selected as a POHC
Chloroform	61	10	44	Group 1; common lab solvent.
Trichlorofluoromethane	24	1	NL[f]	Lower limit of acceptable boiling point range
Vinyl chloride	-12	58	26	Group 1; potential breakthrough problem

[A] A ranking of 1 is the most difficult to incinerate.

[b] The general target range in the VOST Protocol is 30° to 100°C.

[c] Based on the heat of combustion table for 283 RCRA Appendix VIII constituents.

[d] Based on the temperature required to achieve 99.99 percent destruction at a residence time of two seconds (list of 55 compounds compiled by J. J. Cudahy of IT Enviroscience, September 1983).

[e] Group number refers to the QAD gas cylinder audit program.

[f] Not listed.

TABLE II. SUMMARY OF PRECISION, ACCURACY, AND TRAIN-TYPE COMPARISON RESULTS[a]

Nominal test conditions	Parameter	Vinyl chloride		Trichloro-fluoro-methane		Chloroform		Carbon tetra-chloride		Benzene		Tetrachloro-ethylene	
	Trap type	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST
0.5 ppb, dry[b]	$\bar{x}_c$, ng/liter	0.60	0.17	2.22	2.37	1.90	1.94	2.22	2.28	2.87	2.55	3.69	3.91
	σ, ng/liter	0.09	0.01	0.31	1.42	0.08	0.11	0.14	0.26	1.04	1.13	0.03	1.79
	% RSD[c]	15.0	5.9	13.9	55.9	4.2	5.7	5.1	11.4	36.2	44.3	0.8	45.8
	% EV[d]	42	12	78	83	83	85	85	71	175	155	103	109
Significant difference?[e]		Yes		No		No		Yes		No		No	
0.5 ppb, wet[f]	$\bar{x}$, ng/liter	0.53	0.36	2.74	2.53	2.02	1.84	2.71	1.63	2.48	2.01	3.79	3.55
	σ, ng/liter	0.13	0.09	0.17	1.0	0.12	0.27	0.39	0.32	0.75	0.03	0.15	0.40
	% RSD	24.5	25.0	6.2	39.5	5.9	14.7	14.4	19.6	30.2	1.5	4.0	11.3
	% EV	38	26	97	89	89	81	85	51	153	124	107	100
Significant difference?[g]		Yes		No		No		Yes		No		No	
15 ppb, dry[h]	$\bar{x}$, ng/liter	38.55	5.25	63.79	46.78	79.73	73.03	88.23	75.55	57.03	53.01	130.2	117.1
	σ, ng/liter	2.89	2.18	3.47	7.93	18.68	2.19	24.64	3.10	15.12	2.20	32.02	10.51
	% RSD	7.5	41.5	6.3	17.0	23.4	3.0	27.9	4.1	26.5	4.2	24.6	9.0
	% EV	91	12	76	56	116	106	92	78	116	107	121	108
Significant difference?[e]		Yes		Yes		No		No		No		No	
15 ppb, wet[i]	$\bar{x}$, ng/liter	20.32	19.98	64.47	33.84	73.34	65.31	86.46	53.43	52.64	49.35	143.4	139.2
	σ, ng/liter	2.10	3.71	4.55	6.62	2.89	6.12	1.13	2.39	1.10	3.45	4.16	3.51
	% RSD	10.3	18.6	7.1	19.6	3.9	9.4	1.3	4.5	2.1	7.0	2.9	2.5
	% EV	48	47	75	39	107	95	90	56	107	100	133	129
Significant difference?[g]		No		Yes		Yes		Yes		No		No	

[a] Includes data from quad Runs Q1 through Q3 and Q6 through Q8 and paired Runs W1 through W8. No data are corrected for blank values.

[b] Quad Runs Q6 through Q8, including all data except Run Q7, Sample No. L.5ST112 values for all compounds.

[c] Standard and relative standard deviations are pooled from paired run data.

[d] Percent of expected value = $(\bar{x}/EV) \times 100$, where EV is the average for applicable runs taken from the summary table of dilution system data and expected concentrations in ng/liter.

[e] Difference between train types based on analysis of variance at 10% probability level.

[f] Paired Runs W5 through W8, including all data. The moisture content of the sampled gas stream was approximately 30%.

[g] Based on t-test statistic at 10% probability level, difference between train types.

[h] Quad Runs Q1 through Q3, including all data except Run Q2, Sample No. L15ND321 values for vinyl chloride and trichlorofluoromethane.

[i] Paired Runs W1 through W4, including all data. The moisture content of the sampled gas stream was approximately 30%.

TABLE III. SUMMARY OF SAMPLE HOLDING TIME RESULTS[a]

Sample holding time[b] (weeks)	Parameter	Vinyl chloride		Trichloro-fluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetrachloro-ethylene	
	Trap type	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST
<1[c]	$\bar{x}_d$ ng/liter	38.55	5.25	63.79	46.78	79.73	73.03	88.23	75.55	57.03	53.01	130.2	117.1
	σ, ng/liter	2.89	2.18	3.47	7.93	18.68	2.19	24.64	3.10	15.12	2.20	32.02	10.5
	% RSD[d]	7.5	41.5	6.3	17.0	23.4	3.0	27.9	4.1	26.5	4.2	24.6	9.0
2[e]	$\bar{x}$, ng/liter	15.21	7.28	47.56	31.16	70.72	67.74	75.55	72.33	53.04	47.80	116.0	99.5
	σ, ng/liter	2.11	0.23	4.29	2.25	0.76	9.19	0.18	6.29	3.31	2.65	2.19	7.50
	% RSD	13.9	3.2	9.0	7.2	1.1	13.6	0.5	8.7	6.2	5.5	1.9	7.5
Difference,[f] %		-61	39	-25	-33	-11	-7	-14	-4	-7	-10	-11	-15
5[g]	$\bar{x}$, ng/liter	10.70	6.42	50.02	29.60	70.42	68.26	81.86	70.29	50.68	50.20	126.1	112.2
	σ, ng/liter	5.64	5.03	0.40	4.64	6.02	5.20	3.09	3.27	1.28	1.02	20.93	12.30
	% RSD	52.7	78.3	0.8	15.7	8.5	7.6	3.8	4.7	2.5	2.0	16.6	11.0
Difference,[f] %		-72	22	-22	-37	-12	-7	-7	-7	-11	-5	-3	-4
Significant difference ?[h]		Yes[i]		Yes		No		No		No		No	

[a] All samples collected at a nominal target compound concentration of 15 ppb in a dry gas stream. All data were used from Runs 01 through 05 except for Run 02, Sample No. L15ND121 values for vinyl chloride and trichlorofluoromethane. No data are corrected for blank values.

[b] Time between sample collection and analysis. All samples were stored in refrigerated cans containing charcoal.

[c] Runs 01 through 03.

[d] Standard and relative standard deviations are pooled from paired run data.

[e] Run 04.

[f] Difference between mean concentrations at indicated holding time and initial values,

$$\% = \frac{\bar{x}\,i - \bar{x}\ \text{initial}}{\bar{x}\ \text{initial}} \times 100$$

[g] Run 05.

[h] Difference between holding times based on analysis of variance at 10% probability.

[i] The effect of sample holding time is significant for the ND train but not for the ST train.